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ORIGINAL RESEARCH

X-ray crystal structures of *p*-halogenated 6,6-diphenylfulvenes

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Abstract Crystal structures of a series of *p*-halogenated 6,6-diphenylfulvenes **2–5** are reported and comparatively discussed including the known structure of the non-halogenate parent compound **1**. The molecular structures show twisted conformations of the plane aryl and fulvene subunits against each other, rather unaffected by the different halogen substituents. The packing structures exclusively involve C–H···X (X = F, Cl, π) contacts while Hal···Hal and π-stacking interactions do not occur.

Keywords 6,6-Diphenylfulvenes · Halogen compounds · X-ray analysis · Supramolecular interactions

Introduction

Fulvenes, being the condensation products of 1,3-cyclopentadiene with aldehydes or ketones are a very interesting class of compounds [1]. Due to their structure featuring three cross-conjugated double bonds, they are distinguished by a particular electronic system that can be regarded as valence isomeric benzoid [2]. Referring to this property, fulvenes have extensively been studied to show their behaviour as organic ligands [3–8]. In this respect, a great variety of organometallic complexes were found differing in the modes of binding, i.e. whether the metal centre is coordinated in ene, diene or triene fashion. For reasons of stability, 6,6-diaryl substituted derivatives of the fulvene are the species normally being investigated in this regard. Also, as previously demonstrated [9], 6,6-diarylfulvenes have proven suitable diene components in Diels–Alder reactions [10].

Despite the broad interest in this substance class, X-ray crystal structures of respective compounds are rare and excepting the metal complexes [3–8] only the crystal structure of the 6,6-diphenylfulvene (**1**) (Fig. 1) has been described [8] and duplicated [11] in the literature. Under these circumstances and to arrive at potential conclusions relating to crystal engineering aspects [12, 13], we determined the crystal structures of a series of differently *p*-halogenated 6,6-diphenylfulvenes **2–5** (Fig. 1). In comparison with the parent compound **1** [8, 11], the structures of **2–5** will give information about the influence of halogen substitution on the molecular and packing structures in this system of compounds that might be applicable to compounds of similar structures.

Experimental

Chemical synthesis

General remarks

Melting points were measured on a microscope heating stage PHMK Rapido (Wägetechnik Dresden). IR spectra were obtained from a Nicolet FT-IR 510 spectrometer as KBr pellet. ^1H and ^{13}C NMR spectra were recorded on Bruker Avance III 500 at 500.1 and 125.8 MHz, respectively, using TMS as reference. Chemical shifts for proton and carbon resonances are reported in ppm (δ). Solvents were purified by standard procedures [14].

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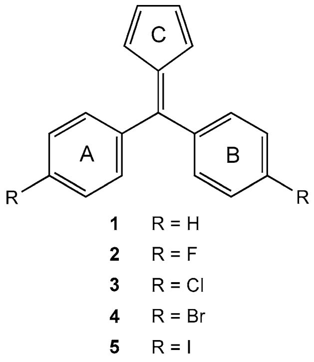

Fig. 1 Chemical structures of the diarylfulvens studied, with designation of ring planes

4,4′-Dibromobenzophenone was prepared from bromobenzene and carbon tetrachloride as described in literature [15]. 4,4′-Diiodobenzophenone was analogously synthesized [15] from iodobenzene and carbon tetrachloride. 4,4′-Difluorobenzophenone, 4,4′-dichlorobenzophenone and dicyclopentadiene were purchased from Acros.

*General procedure for preparation of fulvenes **2–5***

The halogenated diphenylfulvenes **2–5** were obtained from reaction of the respective benzophenone and freshly distilled 1,3-cyclopentadiene (from dicyclopentadiene) in a freshly produced sodium ethanolate solution using the

Table 1 Crystallographic data for the compounds studied

Compound	**2**	**3**	**4**	**5**
Empirical formula	$C_{18}H_{12}F_2$	$C_{18}H_{12}Cl_2$	$C_{18}H_{12}Br_2$	$C_{18}H_{12}I_2$
Formula weight (g mol^{-1})	266.28	299.18	388.10	482.08
Temperature (K)	100(2)	93(2)	93(2)	100(2)
Wave length (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system, space group	Monoclinic, $P2_1/n$	Triclinic, P-1	Triclinic, P-1	Triclinic, P-1
Unit cell dimensions				
a (Å)	10.2407(9)	9.5397(2)	9.5268(3)	9.5970(2)
b (Å)	8.6735(8)	11.0405(3)	11.3248(3)	11.6949(3)
c (Å)	14.9909(14)	15.5749(4)	15.6599(4)	15.9312(4)
α (°)	90.00	84.4580(10)	84.3280(10)	84.1990(10)
β (°)	98.316(4)	76.4370(10)	76.509(2)	76.1230(10)
γ (°)	90.00	65.0000(10)	65.2550(10)	66.2450(10)
V (Å^3)	1317.5(2)	1445.24(6)	1492.06(7)	1588.78(7)
Z	4	4	4	4
Calculated density (g m^{-3})	1.342	1.375	1.728	2.015
Absorption coefficient (mm^{-1})	0.096	0.435	5.419	3.946
F(000)	552	616	760	904
Crystal size (mm^3)	0.35 × 0.26 × 0.25	0.60 × 0.40 × 0.30	0.45 × 0.44 × 0.16	0.25 × 0.19 × 0.05
Θ range for data collection (°)	2.26–29.06	1.34–39.43	1.34–35.00	1.32–25.00
Limiting indices	$-11 \leq h \geq 14$	$-17 \leq h \geq 16$	$-15 \leq h \geq 15$	$-11 \leq h \geq 11$
	$-11 \leq k \geq 11$	$-19 \leq k \geq 19$	$-18 \leq k \geq 18$	$-13 \leq k \geq 13$
	$-20 \leq l \geq 20$	$-27 \leq l \geq 27$	$-25 \leq l \geq 25$	$-18 \leq l \geq 16$
Reflections collected/unique	35595/3497 [R(int)] = 0.0421]	83408/17168 [R(int)] = 0.0270]	32223/13118 [R(int)] = 0.0394]	12654/5571 [R(int)] = 0.0270]
Completeness to Θ (%)	99.5	99.4	99.7	99.7
Refinement method	Full-matrix least squares on F^2	Full-matrix least squares on F^2	Full-matrix least squares on F^2	Full-matrix least squares on F^2
No. of F values used [$I > 2\sigma(I)$]	2641	13428	9531	4677
Restraints/parameters	0/181	0/361	0/361	0/361
Goodness-of-fit on F^2	1.061	1.075	1.067	0.987
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0416$,	$R_1 = 0.0371$,	$R_1 = 0.0445$,	$R_1 = 0.0264$,
	$wR_2 = 0.0938$	$wR_2 = 0.1013$	$wR_2 = 0.0891$	$wR_2 = 0.0512$
R indices (all data)	$R_1 = 0.0616$,	$R_1 = 0.0548$,	$R_1 = 0.0722$,	$R_1 = 0.0356$,
	$wR_2 = 0.1025$	$wR_2 = 0.1135$	$wR_2 = 0.0937$	$wR_2 = 0.0542$
Largest diff peak and hole (e Å^{-3})	0.331 and −0.211	0.687 and −0.437	0.850 and −0.939	0.574 and −0.644

method of Thiele [16]. Details for the individual compounds are given below.

6,6-Bis(4-fluorophenyl)fulvene (**2**). Recrystallisation from *n*-hexane yielded 35% bright red crystals (mp 98 °C). Spectroscopic and other analytical data correspond to the specifications from literature [17, 18].

6,6-Bis(4-chlorophenyl)fulvene (**3**). Recrystallisation from ethanol yielded 62% bright red crystals (mp 112 °C). Spectroscopic and other analytical data correspond to the specifications from literature [4, 19, 20].

6,6-Bis(4-bromophenyl)fulvene (**4**). Recrystallisation from ethanol yielded 58% bright red crystals (mp 128–130 °C, lit. [19] mp 128–130 °C). IR (KBr): 3068; 1633; 1582; 1070; 1009; 832. ^{1}H NMR ($CDCl_3$): 7.52 (d, $^{3}J_{HH} = 8.4$ Hz, 4H, H7); 7.16 (d, $^{3}J_{HH} = 8.4$ Hz, 4H, H6); 6.62 (d, $^{3}J_{HH} = 6$ Hz, 2H, H1); 6.22 (d, $^{3}J_{HH} = 6.4$ Hz, 2H, H2). ^{13}C NMR ($CDCl_3$): 148.7 (C4); 144.5 (C3); 139.6 (C5); 133.5 (C6); 133.2 (C2); 131.1 (C7); 123.9 (C1); 123.6 (C8).

6,6-Bis(4-iodophenyl)fulvene (**5**). Recrystallisation from ethanol yielded 9% bright red crystals (mp 138 °C). IR (KBr): 3071; 1579; 1058; 1004; 833. ^{1}H NMR ($CDCl_3$): 7.76 ($^{3}J_{HH} = 10$ Hz, 4H, H7); 7.06 (d, $^{3}J_{HH} = 10$ Hz, 4H, H6); 6.63 (d, $^{3}J_{HH} = 5$ Hz, 2H, H1); 6.26 (d, $^{3}J_{HH} = 5$ Hz, 2H, H2). ^{13}C NMR ($CDCl_3$): 149.1 (C4); 144.5 (C3); 140.2 (C5); 137.2 (C7); 133.8 (C6); 133.3 (C2); 124.0 (C1); 95.7 (C8).

Crystal structure determination

Crystals of the compounds suitable for X-ray analysis were formed by slow evaporation of corresponding solutions of **2**–**5** in ethanol. All crystals were measured on a Bruker Kappa Apex II using graphite-monochromated Mo Ka radiation ($\lambda = 0.71073$ Å). Data collection: SMART; cell refinement: SMART; data reduction: SAINT [21]. Preliminary structure models were derived by Direct Methods using SHELXS-97 [22] and were refined with full-matrix least squares methods against F^2 using SHELXL-97 [22]. All non-hydrogen atoms were refined anisotropically.

Table 2 Dihedral angles of compounds **1**–**5**

Denotation[a]	**1** [11]	**2**	**3**	**4**	**5**
A/B	74.1	71.67(4)	78.90(3)	74.80(7)	80.57(10)
	78.6		76.23(2)	80.08(8)	71.98(13)
A/C	46.30(6)	44.13(6)	56.68(4)	49.20(12)	58.73(15)
	44.74(6)		52.42(3)	57.72(11)	49.56(19)
B/C	57.97(6)	54.46(4)	47.58(3)	53.93(8)	47.82(12)
	53.22(5)		49.05(4)	47.51(10)	53.05(14)

[a] Designations of the ring mean planes in Fig. 1

Table 3 Selected intermolecular hydrogen bonding contacts

Atoms involved[a]	Symmetry	Distance (Å)		Angle (°)
		D(D···A)	d(H···A)	θ(D–H···A)
1 [11]				
C12A–H12A···Cg6	$1 - x, 1 - y, -z$	3.8117	2.91	159
C16–H16···Cg1	$1 - x, -y, 1 - z$	3.5352	2.88	127
C22–H22···Cg2	$1 - x, -y, 1 - z$	3.8584	2.94	163
C26A–H26A···Cg4	$1 - x, 1 - y, -z$	3.4747	2.86	123
2				
C9–H9···F2	$1 - x, 1 - y, 2 - z$	3.4508(16)	2.56	157
C15–H15···F2	$1 - x, 2 - y, 2 - z$	3.2701(14)	2.48	141
C6–H6···Cg1	$-x, -y, -z$	3.4477(14)	2.81	125
C12–H12···Cg1	$-x, -y, -z$	3.7006(13)	2.81	157
3				
C18–H18···Cl2	$x, -1 + y, z$	3.7795(9)	2.85	168
C33–H33···Cl3	$1 + x, -1 + y, z$	3.8364(9)	2.90	169
C9–H9···Cg1	$x, 1 - y, 1 - z$	3.7554(17)	2.99	140
C21–H21···Cg3	$1 - x, 2 - y, -z$	3.5265(16)	2.75	142
4				
C21–H21···Cg3	$1 - x, 2 - y, -z$	3.819(3)	2.94	154
C23–H23···Cg3	$-x, 2 - y, -z$	3.527(3)	2.72	143
5				
C3–H3···Cg1	$1 - x, 1 - y, 1 - z$	3.611(6)	2.78	146
C5–H5···Cg1	$-x, 1 - y, 1 - z$	3.786(5)	2.91	153

[a] Cg1 is defined as the centre of the ring with C14–C18, Cg3 is defined as the centre of the ring with C32–C36, Cg4 is defined as the centre of the ring with C32–C36

Multiscan absorption corrections were applied using the SADABS program [23]. All non-hydrogen atoms were refined anisotropically. Geometrical calculations were performed using PLATON [24] and molecular graphics were generated using Ortep-3 [25] and SHELXTL [22].

Results and discussion

Crystallization of the halogenated diphenylfulvenes **2**–**5** (Fig. 1) from ethanol solution yielded solvent-free species. Crystal data and details of the refinement of the structures **2**–**5** are summarized in Table 1. Selected torsion angles for the diphenylfulvene derivatives that define the principal molecular conformations are listed in Table 2. Parameters of the weak intermolecular interactions are specified in Table 3. Molecular structures **2**–**5**, including atom labelling schemes and ring specification are shown in Fig. 2, while packing illustrations and diagrams involving specific modes of C–H···X interactions are given in Figs. 3, 4, and 5.

Structures of halogenated diphenylfulvenes **2**–**5**

In contrast to the fluorinated diphenylfulvene **2**, which crystallizes in the monoclinic space group $P2_1/n$ with one molecule in the asymmetric unit, all the other examined fulvenes **3**–**5**, and including the parent fulvene **1** [11] were found to crystallizes with two molecules per asymmetric unit in the triclinic space group *P*-1. Without exceptions, both the phenyl rings (A, B) and the cyclopentadienyl unit (C) of the molecular structures are planar not deviating significantly from the least-squares plane of the rings (Table 2). Considering the bond lengths of the cylopentadienyl ring, this unit presents itself more like a 1,4-diene than an aromatic system. Bolte and Amon [11] found that the dihedral angles involving the planes of fulvene (C) and phenyl rings (A, B) are 46.30° and 57.97° for one molecule and 44.74°, 53.22° for another one. The present halogenated diphenylfulvenes behave similar in this respect. Namely, the torsion angles including the aryl rings and the fulvene unit range between 44.14° (compound **2**) and 49.56° (compound **5**) for the one aryl ring, and from

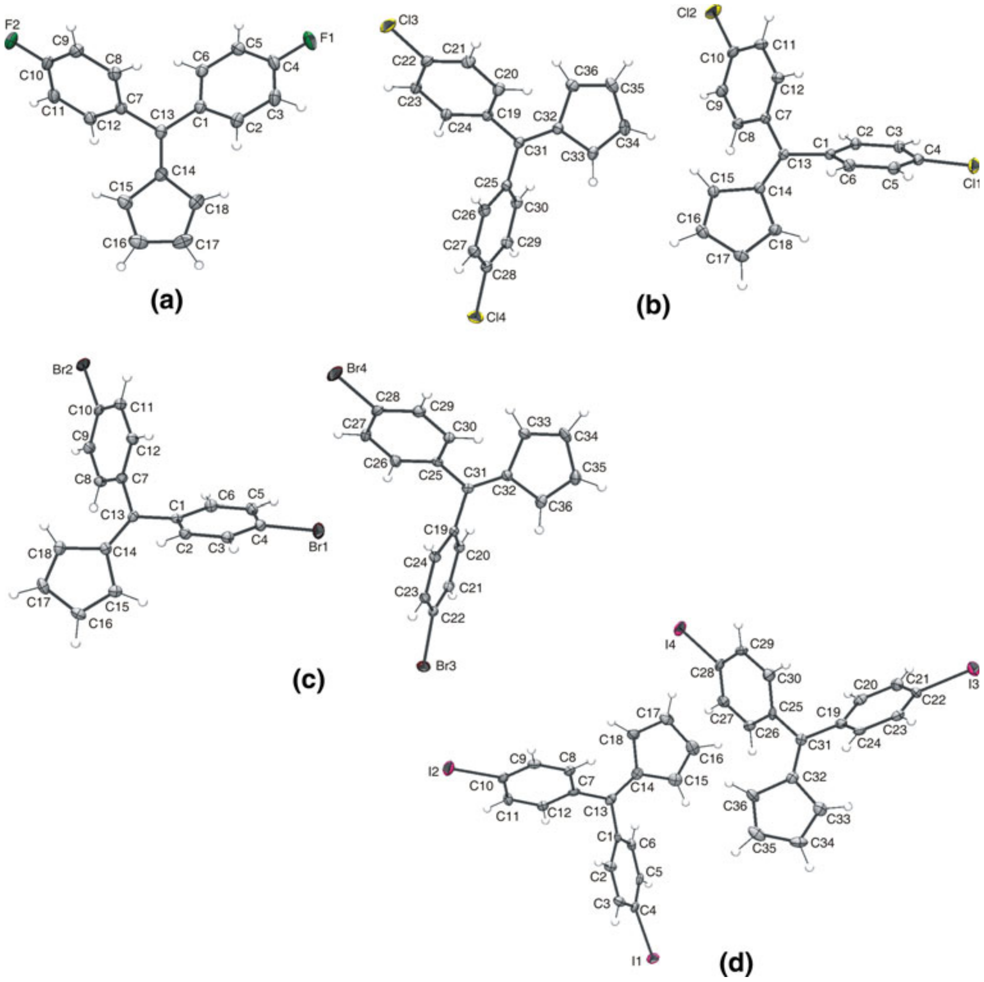

Fig. 2 Perspective views of **2** (**a**), **3** (**b**), **4** (**c**) and **5** (**d**), including atom numbering scheme. Thermal ellipsoids are at 50% probability level

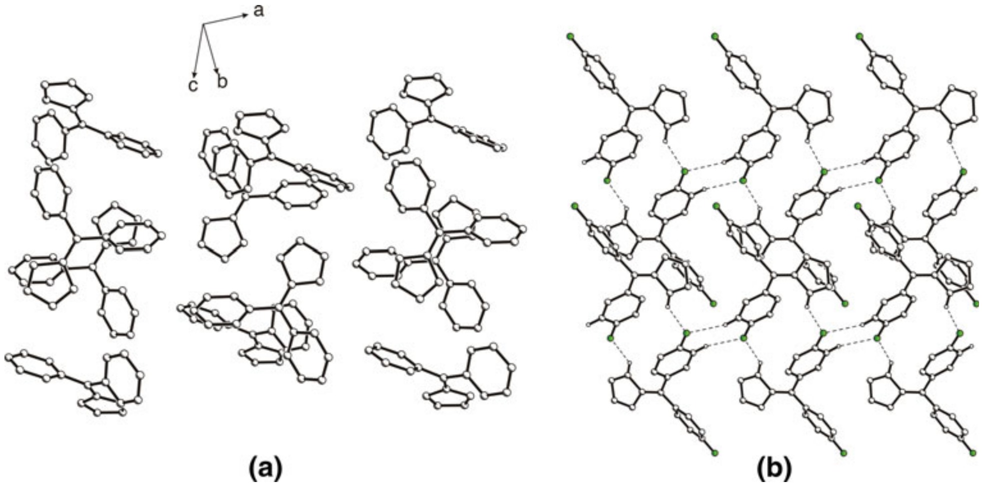

Fig. 3 Crystalline packings of **1** (**a**) and **2** (**b**) viewed down the crystallographic *c*-axis. Noncovalent C–H···F interactions are represented as *broken lines*. Non-relevant hydrogen atoms are omitted for clarity

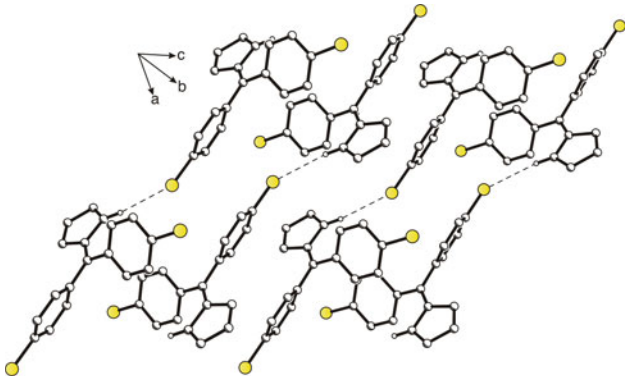

Fig. 4 Crystalline packing of **3** showing the noncovalent C–H···Cl interactions represented as broken lines. Non-relevant hydrogen atoms are omitted for clarity

52.42° (compound **3**) to 58.73° (compound **5**) for the other. Hence, in no case we see coplanarity of the rings including the fulvene moiety, suggesting missing conjugation of the π-systems.

Although the framework of the parent 6,6-diphenylfulvene **1** is composed of three π-electron containing plane subunits, though twisted against each other, π-stacking interactions [26] between adjacent molecules are absent in the crystal structure [11], whereas the packing of **1** is dominated by several C–H···π contacts [27]. In the same way behaves the compound **2** since there is no close intermolecular distance in the crystal structure (closest distance between adjacent aryl rings 4.7 Å) that would indicate a π-stacking interaction [26]. Instead, a weak bifurcated C–H···F contact [9] ($d = 2.56$ Å, $\theta = 157^\circ$, $d = 2.48$ Å, $\theta = 141^\circ$) leads to a zigzag chain along the crystallographic *b*-axis. In addition, C–H···π interactions [27] connect the zigzag chains to a molecular network and stabilize the crystal structure of the compound **2**.

Substitution of the fluorine atoms in **2** for chlorine in the molecule **3** does not involve significant changes in the crystal structure. As before, none of the aryl rings of **3** is included in π-stacking interaction, but several C–H···π contacts are found. Moreover, two weak C–H···Cl

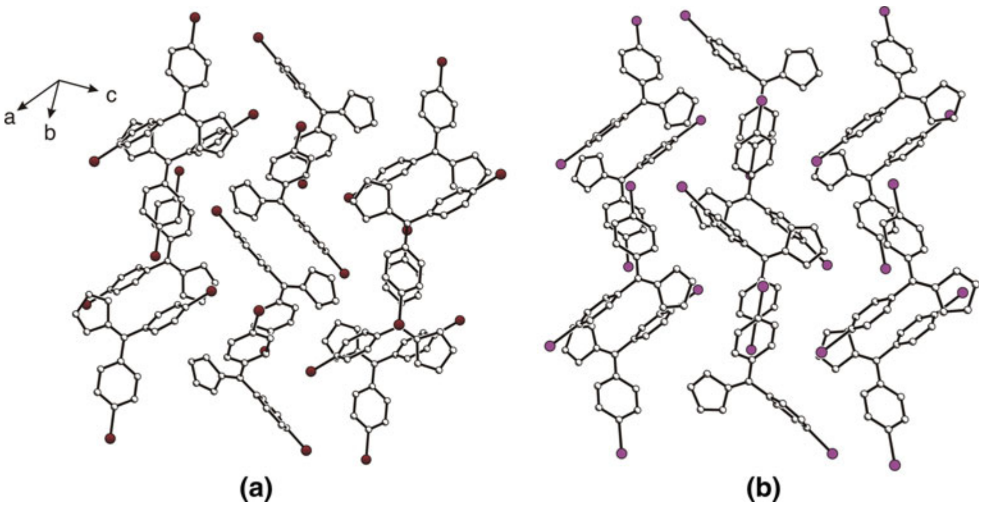

Fig. 5 Crystalline packing of **4** (**a**) and **5** (**b**) viewed down the crystallographic *a*-axis. All hydrogen atoms are omitted for clarity

contacts [28, 29] lead to chain formations in the crystal structure, one being along the crystallographic *b*-axis, the other one parallel to the *ab* plane. However, a remarkable fact of the crystal structure of **3** is the absence of an inter-halogen contact [30, 31] which is often found in the structure of similar chloro containing compounds [32–34].

Even in the structure of **4**, referring to *p*-bromo substituted diphenylfulvene, there is no inter-halogen contact, although this type of Br···Br interaction, both in *head-on* and *side-on* mode [30, 31], is rather frequent for related compounds [34–37]. Actually, the bromine atoms of **4** are not involved in any relevant contacts including C–H···Hal as before. Only several weak C–H···π contacts are shown to stabilize the crystal packing. The crystal structure of the iodo derivative **5** is very similar to **4**, also having only C–H···π contacts for stabilization and lacking halogen involved contacts.

Conclusion

A series of 6,6-diphenylfulvenes **2**–**5** featuring fluorine, chlorine, bromine and iodine substituents in the *p*-positions of the aryl rings, respectively, and including also the unsubstituted parent molecule **1** as a compound of comparison, have been demonstrated to show solid-state molecular structures with twisted conformations of the plane subunits against each other that are not much affected by the different halogen substituents. Even though the molecules **1**–**5** are exclusively composed of π-electron containing planar moieties, interactions classed with π-stacking contacts [26] are missing in the crystal structures. Also, as another unusual finding, none of the structures involve a relevant halogen···halogen contact [30, 31]. This is a rather uncommon behaviour since none of the molecules dispose of a competing polar functionality (oxygen or nitrogen donor atoms). Only in the cases of **2** and **3**, i.e. the fluoro and chloro derivatives, weak C–H···F and C–H···Cl contacts [29], respectively, are found, while corresponding C–H···Br and C–H···I contacts do not occur in the structures of **4** and **5**. Hence, the crystal structures of the compounds **2**–**5**, and in particular of **4** and **5**, are rather unexpected compared to similar compounds where π-stacking and halogen···halogen contacts are the modes of interaction largely dominating the packing structures. Therefore, the conclusion is that molecules both simple in their constitution and rather defined in conformation may not necessarily make use of the typical supramolecular synthons [38], such as π-stacking and halogen···halogen interaction, deduced from the molecular construction to form the crystal structure. This is a problem seriously interfering with common aspects of crystal engineering [12, 13].

Supplementary data

CCDC 784790 (**2**), 784788 (**3**), 784789 (**4**) and 784791 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/data_request/cif [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033; e-mail: deposit@ccdc.cam.ac.uk].

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